

SILICON WAFER FOR SOLAR CELLS AND METHOD FOR PRODUCING SAME

TECHNICAL FIELD OF THE INVENTION

[0001] The present invention relates to a silicon wafer for solar cells made by slicing a silicon ingot employing fixed abrasive grain slicing and a method for producing same.

BACKGROUND OF THE INVENTION

[0002] From the viewpoint of energy resource depletion problems and environmental problems, practical use of solar cells has progressed as a new energy resource. In terms of solar cells to be used in the new energy resource, solar cells, in which a p-n junction is formed on a light-receiving surface of a silicon wafer by diffusion of impurities and an electrode is each formed on the light-receiving surface and a rear surface opposite to the light-receiving surface, are main stream.

[0003] Silicon wafers to be used for such solar cells employing solar battery cells are made by slicing silicon ingots and then a surface thereof is surface-treated.

[0004] A wire saw is generally used for slicing a silicon ingot. Examples of types for wire saws include a free abrasive grain wire saw configured to cause a wire to travel with the wire pressing to silicon ingots while supplying the wire with a slurry of abrasive grains (for instance, JP 2012-24866 A) and a fixed abrasive grain wire saw configured to cause a wire to travel with the wire

pressing to silicon ingots by use of a saw wire where abrasive grains are fixed to a surface of a core wire (for instance, JP 2013-12688 A and JP 2013-43268 A).

[0005] Examples of saw wires to be used for fixed abrasive grain wire saws include resin bond-wires each having a surface of a core wire onto which abrasive grains are fixed with an adhesive resin (for instance, JP 2000-052226 A) and electrodeposition wires where abrasive grains are fixed to a surface of a core wire by electrodeposition via a plating layer (for instance, JP 2011-255475 A).

[0006] A surface treatment is carried out on each surface of slice pieces obtained by slicing the silicon ingot by etching to make each surface of the slice pieces in a preferable shape. As well as removal of affected flow layers formed on surfaces of the slice pieces by etching, fine uneven parts are formed on each of the surfaces of the slice pieces. Light is multiply reflected on a wafer surface due to such uneven parts, leading to an increase in absorption of light as well as a reduction of reflectance. As a result, it becomes possible to effectively utilize incident light.

[0007] However, a materially changed surface layer, in other words, an affected flow layer accompanied by destruction and disordering of a crystal structure, polycrystallization, amorphousization, and microscopically stacking fault is formed on a silicon wafer by slice

processing along with mechanical and thermal action. As a result, distortion and stress remain in the portion.

[0008] In the free abrasive grain slicing, the affected flow layer caused by slicing a slice piece surface has a thickness of about 10 μm to 20 μm , which is relatively great. In view of easy generation of etching from a portion having great distortion and residual stress, effects obtained by etching are easily obtainable. That is, uneven parts are formed by removing the affected flow layer by etching.

[0009] The fixed abrasive grain slicing has a great advantage that material yield is improved because of having a relative small cutting kerf loss of ingots by slicing compared with the free abrasive grain slicing. In the fixed abrasive grain slicing, however, a slice piece sliced has an affected flow layer formed on a surface of the slice piece with a thickness of less than 10 μm , which is relatively small. Accordingly, a problem that uneven parts, which are sufficient for lowering the reflectance by etching, are not easily formed, has been pointed out.

[0010] In addition, surface unevenness formed by etching the slice piece made of polycrystalline silicon is random in crystal orientations of crystal grains exposed. This arises a problem that uneven brightness (difference of crystal grain contrast) of a surface of a wafer which has different brightness is caused by the difference in solution speed on a crystal surface. This results in a

cause of appearance failure when producing solar battery cells.

[0011] In recent years, use of polycrystalline silicon has increased from a point of production cost because of improvement of performance of polycrystalline silicon, although a silicon ingot made of a monocrystalline silicon has been generally used.

[0012] With reference to etching, etching with an etching solution containing hydrofluoric acid, nitric acid, and sulfuric acid relative to a slice piece made of a monocrystalline silicon has been disclosed (for instance, WO 2005/036629 A1, JP 2004-503081 A, JP 09-270400 A, JP 2004-063954 A). Further, etching with a mixed solution of hydrofluoric acid and nitric acid relative to a slice piece made of polycrystalline silicon has been disclosed (for instance, JP 2006-73832 A). No etching methods for sufficiently lowering a reflectance and generating no uneven brightness on a surface of a wafer caused by the difference in the size and shape in the crystal grains for etching of a slice piece made of polycrystalline silicon, more specifically, etching of a slice piece sliced by the fixed abrasive grain slicing, have currently been found.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0013] Patent document 1: JP 2012-24866 A

Patent document 2: JP 2013-12688 A

Patent document 3: JP 2013-43268 A
Patent document 4: JP 2000-052226 A
Patent document 5: JP 2011-255475 A
Patent document 6: WO 2005/036629 A1
Patent document 7: JP 2004-503081 A
Patent document 8: JP 09-270400 A
Patent document 9: JP 2004-63954 A
Patent document 10: JP 2006-73832 A

SUMMARY

PROBLEMS TO BE SOLVED

[0014] The present disclosure has been made in view of the aforementioned actual situation. It is an object of the present disclosure to provide a silicon wafer for solar cells having a low reflectance and less uneven brightness made by using a slice piece obtained by slicing polycrystalline silicon ingots employing fixed abrasive grain slicing and a production method thereof.

MEANS FOR SOLVING THE PROBLEMS

[0015] The inventors of the present disclosure have found out that it is possible to obtain a silicon wafer for solar cells having a low reflectance and less uneven brightness by etching a polycrystalline silicon slice piece sliced by a fixed abrasive grain wire saw by use of a specific etching solution to reach the present invention. More specifically, the present disclosure relates to a method for

producing a silicon wafer for solar cells which comprises the step of etching a polycrystalline silicon slice piece sliced by a fixed abrasive grain wire saw with an etching solution containing mixed acid composed of hydrofluoric acid, nitric acid, and sulfuric acid at a specific ratio.

[0016] The summary of the present disclosure is described as below.

According to the present disclosure, there is provided a method for producing a silicon wafer for solar cells which includes the step of etching a slice piece made of polycrystalline silicon with an etching solution consisting essentially of mixed acid, wherein the slice piece is sliced by a fixed abrasive grain wire saw, the mixed acid is composed of hydrofluoric acid represented by chemical formula HF , nitric acid represented by chemical formula HNO_3 , and sulfuric acid represented by chemical formula H_2SO_4 , a composition range of the mixed acid is within a region surrounded by four line segments for connecting points in the sequence set forth in a triangular diagram that expresses the composition in weight %, the points include: point A, in which the hydrofluoric acid is 2.82 weight %, the nitric acid is 0.18 weight %, and the sulfuric acid is 97 weight %; point B, in which the hydrofluoric acid is 0.18 weight %, the nitric acid is 2.82 weight %, and the sulfuric acid is 97 weight %; point C, in which the hydrofluoric acid is 8.47 weight %, the nitric acid is 0.53 weight %, and the sulfuric acid is 91

weight %; and point D, in which the hydrofluoric acid is 0.53 weight %, the nitric acid is 8.47 weight %, and the sulfuric acid is 91 weight %, wherein the etching solution has a water concentration of 0 weight % to 10.5 weight %.

[0016a] The present disclosure provides a method for producing a silicon wafer for solar cells, comprising the step of etching a slice piece obtained by slicing polycrystalline silicon using a fixed abrasive grain wire saw with an etching solution consisting essentially of mixed acid, the mixed acid is composed of hydrofluoric acid represented by chemical formula HF , nitric acid represented by chemical formula HNO_3 , and sulfuric acid represented by chemical formula H_2SO_4 ,

a composition range of the mixed acid is within a region surrounded by four line segments connected in the sequence set forth in a triangular diagram that expresses the composition in weight %, the four line segments comprising:

point A, in which the hydrofluoric acid is 2.82 weight %, the nitric acid is 0.18 weight %, and the sulfuric acid is 97 weight %;

point B, in which the hydrofluoric acid is 0.18 weight %, the nitric acid is 2.82 weight %, and the sulfuric acid is 97 weight %;

point C, in which the hydrofluoric acid is 8.47 weight %, the nitric acid is 0.53 weight %, and the sulfuric acid is 91 weight %; and

point D, in which the hydrofluoric acid is 0.53 weight %, the nitride acid is 8.47 weight %, and the sulfuric acid is 91 weight %, and

wherein the etching solution has a water concentration of 0 weight % to 10.5 weight %,

a surface of the silicon wafer has uneven parts formed of a plurality of bowl bottom-shaped concave holes formed on throughout the whole area of the surface thereof by etching the slice piece made of polycrystalline silicon obtained by being sliced by the fixed abrasive grain wire saw with the etching solution,

the plurality of concave holes each have an opening diameter of 2 μm to 15 μm , and

a plurality of fine holes each have an opening diameter of 0.1 μm to 1.5 μm formed on inner walls of the concave holes.

[0017] In the method for producing a silicon wafer for solar cells, particularly in the case where the slice piece is a polycrystalline silicon wafer sliced by a resin-bond wire saw, a silicon wafer for solar cells having a low reflectance and less brightness unevenness is obtainable.

According to the method for producing a silicon wafer for solar cells, a silicon wafer for solar cells, in which a surface of the silicon wafer has uneven parts formed of a plurality of bowl bottom-shaped concave holes, the plurality of concave holes

each have an opening diameter of 2 μm to 15 μm , and a plurality of fine holes each have an opening diameter of 0.1 μm to 1.5 μm formed on inner walls of the concave holes, is obtainable.

In the method for producing a silicon wafer for solar cells, the etching solution is to be used for etching the slice piece made of polycrystalline silicon sliced by the fixed abrasive grain wire saw, the etching solution consists essentially of mixed acid, the mixed acid is composed of hydrofluoric acid represented by a chemical formula HF , nitric acid represented by a chemical formula HNO_3 , and sulfuric acid represented by a chemical formula H_2SO_4 , a composition range of the mixed acid is within a region surrounded by four line segments for connecting

points in the sequence set forth in a triangular diagram that expresses the composition in weight %, the points include: point A, in which the hydrofluoric acid is 2.82 weight %, the nitric acid is 0.18 weight %, and the sulfuric acid is 97 weight %; point B, in which the hydrofluoric acid is 0.18 weight %, the nitric acid is 2.82 weight %, and the sulfuric acid is 97 weight %; point C, in which the hydrofluoric acid is 8.47 weight %, the nitric acid is 0.53 weight %, and the sulfuric acid is 91 weight %; and point D, in which the hydrofluoric acid is 0.53 weight %, the nitride acid is 8.47 weight %, and the sulfuric acid is 91 weight %, and the etching solution has a water concentration of 0 weight % to 10.5 weight %. The etching solution has a temperature of 0°C to 45°C when the etching is conducted.

[0018] In the etching solution, a saw wire to be used for the fixed abrasive grain wire saw may be a resin-bond wire saw.

ADVANTAGES

[0019] The present disclosure provides a silicon wafer for solar cells having a low reflectance and less bright unevenness made by the use of a slice piece obtained by slicing a polycrystalline silicon ingot employing fixed abrasive grain slicing and a method for producing thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020]

FIG. 1 is a triangular diagram for illustrating composition of an etching solution to be used in the present invention;

FIGS. 2 (a) to 2 (c) respectively show an image of a surface of a silicon wafer for solar cells;

FIGS. 3 (a) to 3 (c) are each an explanatory view of uneven parts of a surface of a silicon wafer for solar cells of the present invention; and

FIGS. 4 (a) to 4 (d) are each an image showing a brightness state of a surface of a silicon wafer for solar cells.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0021] A silicon wafer for solar cells of the present invention is obtainable by etching a slice piece obtained by slicing a polycrystalline silicon ingot employing fixed abrasive grain slicing with an etching solution.

[0022] The fixed abrasive grain slicing is to slice an ingot with a saw wire where abrasive grains are adhered to a surface of a core wire. Examples of the fixed abrasive grain slicing having an aspect of adhering abrasive grains to a surface of a core wire include a molten metal method, an electrodeposition method, and a resin bonding method.

[0023] The molten metal method is a method for fixing abrasive grains to a surface of a core wire via a low-melting metal such as solder alloy. The method described

in JP 2010-201602 A exemplifies this method.

[0024] The electrodeposition method is a method for fixing abrasive grains to a surface of a core wire via a plating layer by forming the plating layer on the surface of the core wire with a plating liquid mixed with abrasive grains. JP 2003-340729 A exemplifies this method.

[0025] The resin bonding method is a method for fixing abrasive grains to a surface of a core wire via a resin adhesion.

[0026] A steel wire is preferably used as a core wire to be used in the fixed abrasive grain slicing. While the wire diameter is not particularly limited, the wire diameter is preferably 0.3 mm to 0.05 mm. Examples of the steel wire include a wire rod of thermal treated spring steel such as high-carbon steel or medium carbon low-alloy steel, a hard steel wire, a piano wire, a stainless wire, a wire rod created by processed spring steel such as a cold-rolled steel wire or an oil temper wire or a steel wire rod with high-toughness and high fatigue strength such as low alloy steel, medium alloy steel, high alloy steel or maraging steel.

[0027] While abrasive grains to be used in fixed abrasive grain slicing are not particularly limited, examples of the abrasive grains include diamond abrasive grains, cubic-based BN abrasive grains, alumina abrasive grains, and silicon carbide abrasive grains. The diamond abrasive grains coated with nickel may be used. More specifically,

the diamond abrasive grains having a diameter of 5 μm to 15 μm are preferably used.

[0028] In the present invention, a silicon wafer for solar cells is produced by etching a slice piece obtained by slicing a polycrystalline silicon ingot with an etching solution employing the fixed abrasive grain slicing.

[0029] The etching solution to be used in the present invention has an essential component of mixed acid composed of hydrofluoric acid (HF), nitric acid (HNO_3), and sulfuric acid (H_2SO_4). This etching solution may further contain water.

[0030] The etching solution may contain organic acid such as aliphatic carboxylic acid, aliphatic sulfonic acid, aliphatic phosphoric acid, and an oxidizing agent such as perchloric acid, perchlorate, perchromic acid, and perchromate as an auxiliary agent. In addition, the etching solution may contain nitrate such as sodium nitrate, potassium nitrate, ammonium nitrate, and nitrite such as sodium nitrite, potassium nitrite, ammonium nitrite, and fluoride salt such as sodium fluoride, potassium fluoride, and ammonium fluoride.

[0031] Each compounding ratio of hydrofluoric acid, nitric acid, and sulfuric acid which comprise a mixed acid relative to the total weight of such acids in the etching solution to be used in the present invention is within the range surrounded by a line segment for connecting a point A (HF: 2.82 weight %, HNO_3 : 0.18 weight %, H_2SO_4 : 97 weight %),

a point B (HF: 0.18 weight %, HNO₃: 2.82 weight %, H₂SO₄: 97 weight %), a point C (HF: 8.47 weight %, HNO₃: 0.53 weight %, H₂SO₄: 91 weight %), a point D (HF: 0.53 weight %, HNO₃: 8.47 weight %, H₂SO₄: 91 weight %) in a triangular diagram shown in FIG. 1.

[0032] The etching solution has a moisture concentration (a weight concentration in the etching solution containing all components that include water, that is, a content of water) of 0 to 10.5 weight %. When the water concentration is higher than this, small recesses are not easily formed, resulting in significant contrast difference of crystal grains of wafers. It is further preferable that the etching solution has a water concentration of 10 weight % or smaller for stability of an etching process.

[0033] A slice piece obtained by slicing a polycrystalline silicon ingot by use of fixed abrasive grain slicing is immersed into an etching solution to conduct etching. Subsequently, the slice piece is rinsed in water. The liquid temperature of the immersion is preferably 0°C to 45°C, and the time that has taken for the immersion is preferably 1 minute to 30 minutes. When the liquid temperature is below this range, the progress of etching is not sufficient, resulting in too much time until uneven parts are formed. When the liquid temperature is above this range, uneven parts, particularly small recesses are not easily formed, resulting in significant contrast difference of crystal grains without sufficient lowering of

the reflectance. As a result, there are contrast differences in brightness, which reduces the commodity value. Accordingly, the liquid temperature is further preferably 5°C to 40°C.

[0034] When each composition ratio of hydrofluoric acid, nitric acid, and sulfuric acid is out of the range surrounded by the line segment to connect the points A,B,C, D in the triangular diagram in the etching solution, etching reaction does not progress due to too slow etching speed. This results in too much time to form uneven parts. Alternatively, small recesses are not easily formed, resulting in significant contrast of the crystal grains without sufficient reduction in reflectance.

[0035] In the etching solution, the concentration of hydrofluoric acid / (concentration of hydrofluoric acid + concentration of nitric acid) is preferably 0.059 to 0.94. When the concentration of hydrofluoric acid in the etching solution is out of this range, as the etching speed is slower, the small recesses are not easily formed. As a result, the reflectance increases, which may make the contrast differences of the crystal grains significant.

[0036] The concentration of sulfuric acid in the etching solution is 91 weight % to 97 weight %. When the concentration of sulfuric acid is below this range, the etching speed is too slow to progress the etching reaction. As a result, it takes too much time to form uneven parts. When the concentration of sulfuric acid in the etching

solution is above this range, small recesses are not easily formed. As a result, there are significant contrast differences of the crystal grains without sufficient reduction in reflectance.

[0037] It is further preferable that each compounding ratio of hydrofluoric acid, nitric acid, sulfuric acid relative to the total weight of these acids in the etching solution to be used in the present invention is within the range surrounded by line segments for connecting the point A' (HF: 2.62 weight %, HNO₃: 0.88 weight %, H₂SO₄: 96.5 weight %), the point B' (HF: 0.88 weight %, HNO₃: 2.62 weight %, H₂SO₄: 96.5 weight %), the point C' (HF: 6.75 weight %, HNO₃: 2.25 weight %, H₂SO₄: 91 weight%), the point D' (HF: 2.25 weight %, HNO₃: 6.75 weight %, H₂SO₄: 91 weight %) in a triangular diagram shown in FIG. 1 to obtain a silicon wafer for solar cells having a low reflectance and less brightness unevenness caused by contrast differences of the crystal grains.

[0038] It is the most preferable that each compounding ratio of hydrofluoric acid, nitric acid, sulfuric acid relative to the total weight of these acids in the etching solution to be used in the present invention is within the range surrounded by line segments for connecting the point A'' (HF: 1.98 weight %, HNO₃: 1.52 weight %, H₂SO₄: 96.5 weight %), the point B'' (HF: 1.44 weight %, HNO₃: 2.06 weight %, H₂SO₄: 96.5 weight %), the point C'' (HF: 5.09 weight %, HNO₃: 3.91 weight %, H₂SO₄: 91 weight%), the point

D" (HF: 3.71 weight %, HNO₃: 5.29 weight %, H₂SO₄: 91 weight %) in a triangular diagram shown in FIG. 1 to obtain a silicon wafer for solar cells having a low reflectance and less brightness unevenness.

[0039] The etching solution to be used in the present invention is obtainable by mixing an aqueous solution of hydrofluoric acid having a concentration of 40 weight % to 55 weight % or higher, an aqueous solution of nitric acid having a concentration of 59 weight % to 75 weight % or higher, and a sulfuric acid preferably having a concentration of 95 weight % to 98 weight % (sulfuric acid of having a concentration $\times$ % is a mixture of sulfuric acid $\times$ weight part and water (100- $\times$)).

[0040] When the slice piece obtained by slicing a polycrystalline silicon ingot employing fixed abrasive grain slicing is etched with an etching solution having such compounding ratios, as shown in FIG. 2 (a), as well as uneven parts are formed on a surface of the slice piece by exposure of crystal grains of silicon after removing an affected flow layer, the surface is further etched to form a bowl-bottom-shaped recess. Uneven parts which are further finer than the uneven parts caused by the recess are formed on an inner surface of the bowl-bottom-shaped recess. This enables to obtain a silicon wafer for solar cells having a small reflectance of the surface thereof. And a silicon wafer for solar cells having less brightness unevenness is obtainable.

[0041] FIG. 2 (a) is a scanning electron microscope image of an irregular state of a surface of a silicon wafer for solar cells according to the present invention. FIG. 2 (b) is a scanning electron microscope image of an irregular state of a surface of a silicon wafer for solar cells made by etching a slice piece made by slicing a polycrystalline silicon ingot employing free abrasive grain slicing with a mixed etching solution composed of only conventional hydrofluoric acid and nitric acid.

[0042] The silicon wafer for solar cells according to the present invention shown in FIG. 2 (a) has uneven parts formed of a plurality of recesses each having a curved surface-state bottom formed on throughout the whole area of a surface of the silicon wafer. The plurality of recesses each have an opening diameter of 2 μm to 15 μm and one or a plurality of fine pores each having an opening diameter of 0.1 μm to 1.5 μm are formed on each inner wall of the recesses. More specifically, the silicon wafer for solar cells of the present invention has uneven parts composed of a plurality of recesses formed on throughout the whole area of a surface of the silicon wafer. And the plurality of recesses each have an opening diameter of 2 μm to 15 μm and each inner wall of the recesses substantially has a shape where one or a plurality of fine pores are formed. It is possible to confirm such an irregular state by use of a scanning confocal laser microscopy or a profile measurement system and the like described in JP 3810749 B2.

[0043] FIGS. 3 (a) to 3 (c) are respectively a schematic view showing an irregular state of a surface of a silicon wafer for solar cells by use of a cross-sectional surface in a thickness direction of the wafer. FIG. 3 (a) is a partially enlarged schematic view of the irregular state of the surface of the silicon wafer for solar cells shown in FIG. 2 (b). FIG. 3 (b) is a partially enlarged schematic view of the irregular state of the surface of the silicon wafer for solar cells shown in FIG. 2 (a). FIG. 3 (c) is a partially enlarged schematic view of FIG. 3 (b). As shown in FIGS. 3 (a) to 3 (c), the silicon wafer for solar cells of the present invention has uneven parts in a state where a small cycle of uneven parts resulting from substantially bowl-shaped small dents (fine pores) 3 formed by erosion with the etching solution are overlapped with a large cycle of uneven parts (a shape of a substantially bowl-bottom concave or a shape in which substantially bowl-bottom concaves are overlapped) resulting from substantially bowl-shaped large dents (recesses in the shape of a bowl-bottom) when enlarged. An upper edge of each large recess 2 has a diameter d_1 of 2 μm to 15 μm and a depth h_1 of 2 μm to 15 μm . An upper edge of each small recess 3 has a diameter d_2 of 0.1 μm to 1.5 μm and a depth h_2 of 0.1 μm to 1.5 μm . A space p of each upper edge of large recesses 2 adjacent each other is 0 μm to 10 μm . There are a plurality of small dents inside one large dent 2. To the contrary, there are few small dents which correspond to the small

dents 3 in FIG. 3 (b) inside the large dents 2 in the surface of the silicon wafer for solar cells made by etching the slice piece obtained by slicing the polycrystalline silicon ingot employing the free abrasive grain slicing indicated by a microscope image shown in FIG. 2 (b). In addition, the reflectance is 30% and thus sufficiently low surface state cannot be formed as compared to FIG. 2 (a) where the etching solution of the present invention is used.

[0044] The expression "throughout the whole area" means that a space among each upper edge of adjacent recesses, that is, there are recesses on a surface of the silicon wafer so that p, which is a space among each upper edge of adjacent recesses, may be 0 μm to 10 μm . These adjacent recesses may be overlapped one another by entering one another.

[0045] The large dents 2 each look like a shape of a recess portion of a bowl and each have a substantially symmetrical shape where a straight line standing perpendicular to a direction of the silicon wafer surface from the deepest portion of the dent, alternatively a flat surface standing perpendicular to a surface direction of the silicon wafer from the deepest point of the dent is a symmetrical surface. This indicates that as well as removal of an affected flow layer having a small thickness of about 5 μm by etching, etching proceeds in a thickness direction of the wafer to form such symmetrical shaped dents. It is possible to

obtain a silicon wafer having less brightness unevenness in which irregular reflected light is not easily generated on the wafer surface. That is, etching with the etching solution of the present invention can be conducted regardless of the presence of the affected flow layer. Accordingly, bowl bottom-shaped recesses in a symmetrical shape relative to the thickness direction are formed on the surface of the wafer.

[0046] The etching solution of the present invention makes it possible to newly form such large dents 2 and small dents 3 together on silicon after the removal of the affected flow layer. In other words, the etching solution of the present invention makes it possible to form the large dents 2 and the small dents 3 together on the surface of the wafer regardless of the presence of the affected flow layer.

[0047] To the contrary, the slice piece obtained by the slicing of a polycrystalline silicon ingot employing the free abrasive grain slicing may have uneven parts on a surface of the silicon wafer caused by crystal grains by simply removing the affected flow layer by etching due to great thickness of the affected flow layer. It is possible to remove the affected flow layer relatively easily by using a conventional etching solution containing hydrofluoric acid and nitric acid. However, thus obtained dents depend on a crystal orientation of the crystal grains and thus the shapes of these dents are irregular and each

have a non-symmetrical shape relative to the thickness direction of the wafer. As a result, irregular reflected light is easily generated on the surface of the wafer and thus the wafer with uneven brightness left is formed. As mentioned above, the conventional etching solution has uneven parts in a process of removing the affected flow layer and does not newly form uneven parts on the silicon after the removal of the affected flow layer. It is difficult to conduct such etching that the small dents 3 are further formed on the silicon after the removal of the affected flow layer with the conventional etching solution.

[0048] In terms of a polycrystalline silicon wafer with a rough crystal surface, a method for forming uneven parts by etching an affected flow layer with a thickness of 10 μm or greater to be removed where chemical etching is conducted in an acidic etching solution consisting essentially of hydrofluoric acid, nitric acid, and phosphoric acid is disclosed (for instance, JP 10-303443 A, JP 4766880 B2). This is because the following reactions proceed:

$$\text{NHO}_3 + \text{H}_2\text{O} + \text{HNO}_2 \rightarrow 2\text{HNO}_2 + 2\text{OH}^- + 2\text{h}^+ \text{ (positive hole)}$$

$$\text{Si} + 4\text{h}^+ \rightarrow \text{Si}^{4+}$$

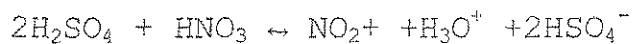
$$\text{Si}^{4+} + 2\text{OH}^- \rightarrow \text{SiO}_2 + \text{H}_2$$

$$\text{SiO}_2 + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + \text{H}_2\text{O}$$

[0049] Accordingly, while reaction speed can be changed and the shape and size of uneven parts are changed according to the ratios of nitric acid for oxidizing silicon and hydrofluoric acid for dissolving silica oxide, sulfuric

acid is preferably added inside system for the purpose of more stable control. The reason for that is described as below.

[0050] More specifically, while the use of concentrated nitric acid only can cause a little oxidization reaction of silicon as indicated in the aforementioned formula, an addition of concentrated sulfuric acid causes base-acid reaction with sulfuric acid as acid and nitric acid as base. As a result, " $\text{-O-SO}_2\text{-OH}$ " anions and " $\text{H}_2\text{O}(+)\text{-NO}_2$ " cations are formed and " $\text{H}_2\text{O}(+)\text{-NO}_2$ " cations are dehydrated, resulting in a great amount of cations (nitronium cations) inside system. That is, a balance inclines righter than the time when condensed sulfuric acid is not added, resulting in faster reaction and control the rough surface of the silicon piece in the reaction formula below.



In view of the aforementioned phenomenon, in the present invention, the concentration of acid to form preferable irregular shapes on the surface of the silicon piece, particularly, the concentration of sulfuric acid has been found out in the present invention.

EXAMPLES

[0051] While examples of the present invention will now be described in detail, the present invention is not limited to these examples.

[0052] Measurements of reflectance of a silicon wafer in

Examples and Comparative Examples were carried out by use of a UV-VIS-NIR Spectrophotometer Solidspec-3700 produced by Shimadzu Corporation and an integrating sphere BIS-3700. An average of values at a wavelength of 600 nm at 9 measurement portions was obtained as a reflectance.

[0053] Example 1

<Silicon ingot>

A polycrystalline silicon ingot produced by Green Energy Technology Inc. was used.

<Saw Wire>

A resin-bonded saw wire (Model No. MW-100-8-16) produced by TKX Corporation was used.

(An adhesive composition for a resin-bonded wire saw: a phenol resin composition

Abrasive grains; diamond wheel: diameter of grinding wheel
8 μm to 16 μm (10.5 μm $\pm$ 1 μm)

Wire: ϕ 100 μm steel wire)

<Slicing process>

A wire saw was wound around a pulley grooved on the periphery thereof and was attached to a cutting device for forming a loop to make a slice piece by traveling the wire at 600 m/minute.

<Etching solution>

Hydrofluoric acid aqueous solution (concentration: 47 wt%):
6.2 weight %

Nitric acid aqueous solution (concentration: 67 wt%): 5.0
weight %

Sulfuric acid aqueous solution at a concentration of 95 wt%: 88.8 weight %

This composition is indicated as a point of Example 1 in FIG. 1.

<Etching>

The slice piece was dipped in an etching solution at 10°C for 20 minutes and was then washed by water to obtain a silicon wafer.

<Characteristics of silicon wafer>

The silicon wafer thus made had a reflectance of 18.6%. And d1 was 3 μm to 12 μm (average 4.8 μm), d2 was 0.1 μm to 1 μm . As an image of a surface state shown in FIG. 4 (a), little brightness unevenness of a surface of the silicon wafer was detected. In addition, FIG. 2 (a) shows a microscopy image of the uneven state of a surface of a silicon wafer.

[0054] Example 2

A silicon wafer was made in the same manner as in Example 1 except for that the composition of the etching solution was: hydrofluoric acid aqueous solution

(concentration: 47 wt%): 6.3 weight %

Nitric acid aqueous solution (concentration: 67 wt%): 4.2 weight %

Sulfuric acid aqueous solution at a concentration of 95 wt%: 89.5 weight %

This composition is indicated as a point of Example 2 in

FIG. 1.

<Characteristics of silicon wafer>

The silicon wafer thus made had a reflectance of 18.0%. And d1 was 3 μm to 10 μm (average: 4.8 μm), d2 was 0.1 μm to 1 μm . Nearly no brightness unevenness of a surface of the silicon wafer was detected.

[0055] Example 3

A silicon wafer was made in the same manner as in Example 1 except for that the composition of the etching solution was: hydrofluoric acid aqueous solution (concentration: 47 wt%): 6.6 weight %
Nitric acid aqueous solution (concentration: 67 wt%): 3.4 weight %
Sulfuric acid aqueous solution at a concentration of 95 wt%: 90 weight %
This composition is indicated as a point of Example 3 in FIG. 1.

<Characteristics of silicon wafer>

The silicon wafer thus made had a reflectance of 20.8%. And d1 was 2 μm to 8 μm (average: 5.4 μm), d2 was 0.1 μm to 1 μm . Nearly no brightness unevenness of a surface of the silicon wafer was detected.

[0056] [Example 4]

A silicon wafer was made in the same manner as in Example 1 except for that the composition of the etching

solution was: a hydrofluoric acid aqueous solution

(concentration: 47 wt%): 6 weight %

Nitric acid aqueous solution (concentration: 67 wt%): 6 weight %

Sulfuric acid aqueous solution at a concentration of 95 wt%: 88 weight %

This composition is indicated as a point of Example 4 in FIG. 1.

<Characteristics of silicon wafer>

The silicon wafer thus made had a reflectance of 21.0%. And d1 was 3 μm to 10 μm (average: 3.9 μm), d2 was 0.1 μm to 0.5 μm . Although a little brightness unevenness of a surface of the silicon wafer was detected, that was not so significant as to damage commercial value.

[0057] Example 5

A silicon wafer was made in the same manner as in Example 1 except for the use of a saw wire by a molten metal method made by the method described in Example 1 of JP 2010-201602 A.

<Production method of wire saw>

A piano wire with a wire diameter of $\Phi 100 \mu\text{m}$ coated with brass was used as a core wire of a wire made from metal.

[0058] Sn-3.0%Ag-0.5%Cu (solidus: 218°C, liquidus: 220°C) was used as a brazing filler material. An aluminum powder (Al) of 0.2% was added to this to be melted.

[0059] A diamond powder coated with nickel was used as abrasive grains 2. Abrasive grains each have a grain diameter of 20 μm to 35 μm . The powder was mixed with organic amine-based activated rosin flux at a ratio of 70:30 (weight %) with respect to the aforementioned brazing filler material and the diamond powder to adjust the viscosity to 300 Pa·s by terpeneol and fill this in a dispenser (syringe) as a paste.

[0060] Subsequently, a dispenser with a nozzle diameter of 100 μm was used to homogeneously apply the paste on the piano core wire having a thickness of 22 μm to 20 μm . The paste was melted by irradiating laser beams having an output of 1 W, diameter of beam 600 μm to 1,300 μm , a wavelength of 808 nm and then natural cooling was conducted.

[0061] Judging the melting state, the ratio of the diamond and the brazing filler material was so set that the thickness of a molten and solidified layer may be within the scope of 5% to 40% of the abrasive grains 2.

[0062] <Characteristics of silicon wafer>

The silicon wafer thus made had a reflectance of 22.0%. And d1 was 3 μm to 14 μm (average: 4.0 μm), d2 was 0.1 μm to 0.5 μm . Although a little brightness unevenness of a surface of the silicon wafer was detected, that was not so significant as to damage commercial value.

[0063] Example 6

A silicon wafer was made by dipping a slice piece in

an etching solution at 25°C for 142 seconds in the same manner as in Example 1 except for that the composition of the etching solution was: hydrofluoric acid aqueous solution (concentration: 47 wt%): 4.2 weight %
Nitric acid aqueous solution (concentration: 69 wt%): 7.8 weight %

Sulfuric acid aqueous solution at a concentration of 95 wt%: 88.0 weight %

This composition is indicated as a point of Example 6 in FIG. 1.

<Characteristics of silicon wafer>

The silicon wafer thus made had a reflectance of 23.0%. And d1 was 2 μm to 12 μm (average: 4.1 μm), d2 was 0.4 μm to 1.0 μm . Although a little brightness unevenness of a surface of the silicon wafer was detected, that was not so significant as to damage commercial value.

[0064] Example 7

A silicon wafer was made by dipping a slice piece in an etching solution at 25°C for 142 seconds and rinsing the slice piece in water in the same manner as in Example 1 except for that the composition of the etching solution was: hydrofluoric acid aqueous solution (concentration: 47 wt%): 4.6 weight %
Nitric acid aqueous solution (concentration: 95 wt%): 6.9 weight %
Sulfuric acid aqueous solution at a concentration of 95

wt%: 88.5 weight %

This composition is indicated as a point of Example 7 in FIG. 1.

<Characteristics of silicon wafer>

The silicon wafer thus made had a reflectance of 19.4%. And d1 was 3 μm to 8 μm (average: 4.8 μm), d2 was 0.4 μm to 1.1 μm . Although a little brightness unevenness of a surface of the silicon wafer was detected, that was not so significant as to damage commercial value.

[0065] Example 8

A silicon wafer was made by dipping a slice piece in an etching solution at 25°C for 142 seconds and rinsing the slice piece in water in the same manner as in Example 1 except for that the composition of the etching solution was: hydrofluoric acid aqueous solution (concentration: 47 wt%): 4.95 weight %

Nitric acid aqueous solution (concentration: 69 wt%): 6.05 weight %

Sulfuric acid aqueous solution at a concentration of 95 wt%: 89.0 weight %

This composition is indicated as a point of Example 8 in FIG. 1.

<Characteristics of silicon wafer>

The silicon wafer thus made had a reflectance of 19.4%. And d1 was 3 μm to 10 μm (average: 6.5 μm), d2 was 0.5 μm to 1.3 μm . Although a little brightness unevenness of a

surface of the silicon wafer was detected, that was not so significant as to damage commercial value.

[0066] Example 9

A silicon wafer was made by dipping a slice piece in an etching solution at 25°C for 142 seconds and rinsing the slice piece in water in the same manner as in Example 1 except for that the composition of the etching solution was: hydrofluoric acid aqueous solution (concentration: 47 wt%): 5.25 weight %

Nitric acid aqueous solution (concentration: 69 wt%): 5.25 weight %

Sulfuric acid aqueous solution at a concentration of 95 wt%: 89.5 weight %

This composition is indicated as a point of Example 9 in FIG. 1.

<Characteristics of silicon wafer>

The silicon wafer thus made had a reflectance of 19.8%. And d1 was 3 μm to 11 μm (average: 5.6 μm), d2 was 0.5 μm to 1.1 μm . There was substantially no brightness unevenness of a surface of the silicon wafer.

[0067] Comparative Example 1

A silicon wafer was made in the same manner as in Example 1 except for that the composition of the etching solution was: hydrofluoric acid aqueous solution (concentration: 47 wt%): 4.5 weight %

Nitric acid aqueous solution (concentration: 67 wt%): 9 weight %

Sulfuric acid aqueous solution at a concentration of 95 wt%: 86.5 weight %

This composition is indicated as a point of Comparative Example 1 in FIG. 1.

<Characteristics of silicon wafer>

The silicon wafer thus made had a reflectance of 26.1%. And d1 was 3 μm to 15 μm (average: 5.1 μm), d2 was 0.1 μm to 1 μm . Brightness unevenness of a surface of the silicon wafer, which was sufficient enough to damage commercial value, was detected. FIG. 4 (b) shows an image to indicate a brightness state of the obtained silicon wafer.

[0068] Comparative Example 2

A silicon wafer was made in the same manner as in Example 1 except for that the composition of the etching solution was: hydrofluoric acid aqueous solution

(concentration: 47 wt%): 3.6 weight %

Nitric acid aqueous solution (concentration: 67 wt%): 16 weight %

Sulfuric acid aqueous solution at a concentration of 95 wt%: 80.4 weight %

<Characteristics of silicon wafer>

The silicon wafer thus made had a reflectance of 27%. Brightness unevenness of a surface of the silicon wafer, which was sufficient enough to damage commercial value, was

detected.

[0069] Comparative Example 3

A silicon wafer was made in the same manner as in Example 1 except for that the composition of the etching solution was: hydrofluoric acid aqueous solution (concentration: 47 wt%): 6 weight %

Nitric acid aqueous solution (concentration: 67 wt%): 29 weight %

Sulfuric acid aqueous solution at a concentration of 95 wt%: 65 weight %

<Characteristics of silicon wafer>

The silicon wafer thus made had a reflectance of 30%. Brightness unevenness of a surface of the silicon wafer, which was sufficient enough to damage commercial value was detected.

[0070] Comparative Example 4

<Slicing process>

A similar ingot as used in Example 1 was sliced by employing the free abrasive grain multi-wire saw slicing. Wire diameter: 0.1 mm (Model No. SRH, produced by JFE Steel Corporation)

Abrasive grains: silicon carbide (Fujimi Incorporated, GC#1500, average particle size: about 8 μm)

Cutting speed: 0.35 mm/minute (ingot feed rate)

Traveling speed of wire: 600 m/minute

<Etching>

A silicon wafer was made by similar etching as in Example 1 except for that the composition of the etching solution was: hydrofluoric acid aqueous solution (concentration: 47 wt%): 25 weight %

Nitric acid aqueous solution (concentration: 67 wt%): 45 weight %

Water: 30 weight %

Etching was conducted at 10°C for two minutes.

<Characteristics of silicon wafer>

It was found that d1 was 10 μm on average and only large dents 2 were admitted and small dents 3 were not admitted. Accordingly, the obtained silicon wafer had a reflectance of 30.8%. FIG. 4(c) shows an image showing a brightness state of the silicon wafer.

[0071] Comparative Example 5

A silicon wafer was made in the same manner as in Example 1 except for that the composition of the etching solution was: hydrofluoric acid aqueous solution (concentration: 47 wt%): 25 weight %

Nitric acid aqueous solution (concentration: 67 wt%): 45 weight %

Water: 30 weight %.

Etching was conducted at 10°C for two minutes.

<Characteristics of silicon wafer>

The silicon wafer thus made had a reflectance of 32.5%,

which was high. FIG. 2 (c) shows an image of an irregular state of a surface of the silicon wafer. FIG. 4 (d) shows an image indicating a brightness state of the silicon wafer. Although d1 was 3 μm to 15 μm (average: 5.5 μm), small dents 3 were not detected. In addition, brightness unevenness of a surface of the silicon wafer, which was sufficient enough to damage commercial value, was detected. The silicon wafer thus made had a reflectance of 32.5%.

INDUSTRIAL APPLICABILITY

[0072] The present invention is a useful technology widely applicable to production of a silicon wafer for solar cells and other photo electric conversion elements.

[0073] Description of Reference Numerals

2: large dent; 3: small dent

CLAIMS

1. A method for producing a silicon wafer for solar cells, comprising the step of etching a slice piece obtained by slicing polycrystalline silicon using a fixed abrasive grain wire saw with an etching solution consisting essentially of mixed acid,

the mixed acid is composed of hydrofluoric acid represented by chemical formula HF, nitric acid represented by chemical formula HNO_3 , and sulfuric acid represented by chemical formula H_2SO_4 ,

a composition range of the mixed acid is within a region surrounded by four line segments connected in the sequence set forth in a triangular diagram that expresses the composition in weight %, the four line segments comprising:

point A, in which the hydrofluoric acid is 2.82 weight %, the nitric acid is 0.18 weight %, and the sulfuric acid is 97 weight %;

point B, in which the hydrofluoric acid is 0.18 weight %, the nitric acid is 2.82 weight %, and the sulfuric acid is 97 weight %;

point C, in which the hydrofluoric acid is 8.47 weight %, the nitric acid is 0.53 weight %, and the sulfuric acid is 91 weight %; and

point D, in which the hydrofluoric acid is 0.53 weight %, the nitride acid is 8.47 weight %, and the sulfuric acid is 91 weight %, and

wherein the etching solution has a water concentration of 0 weight % to 10.5 weight %,

a surface of the silicon wafer has uneven parts formed of a plurality of bowl bottom-shaped concave holes formed on throughout the whole area of the surface thereof by etching the slice piece made of polycrystalline silicon obtained by being sliced by the fixed abrasive grain wire saw with the etching solution,

the plurality of concave holes each have an opening diameter of 2 μm to 15 μm , and

a plurality of fine holes each have an opening diameter of 0.1 μm to 1.5 μm formed on inner walls of the concave holes.

2. The method for producing a silicon wafer for solar cells according to claim 1, wherein a saw wire to be used for the fixed abrasive grain wire saw is a resin-bond wire saw.

3. The method for producing a silicon wafer for solar cells according to claim 1 or claim 2, wherein the etching solution has a temperature of 0°C to 45°C when the etching is conducted.